Reduced Mobility of Elastomers near a Solid Surface As Measured by Neutron Reflectometry

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The effects of an interacting, hydrophobic silicon surface on the interfacial properties of the immiscible polymer blend polybutadiene (PB) and brominated poly(isobutylene-*co*-*p*-methylstyrene) (BIMS) were studied using neutron reflectivity (NR). The results show that an adsorbed polymer layer, approximately $2R_g$ (R_g is the radius of gyration) thick, is always present at the silicon interface. This observation confirms the existence of an immobile gel-like layer which was invoked by numerous authors to explain the reduced dynamics and anomalous rheological properties of polymers at long distances from interactive substrates. The attractive substrate was also shown to affect the equilibrium interfacial width between the immiscible polymers. Narrowing of the interfacial width was observed only when the layer adjacent to the silicon substrate was less than $3R_g$ thick, indicating that only chains in direct contact with the interface were affected.

Introduction

Elastomers are often blended to improve the physical properties of the original materials, to reduce compound cost, and to produce better processing behavior. The ultimate properties of these blends are directly related to the interfacial structure and properties.

In a previous work we measured the interfacial width between two dissimilar elastomers, d6-polybutadiene (dPB) and brominated poly(isobutylene-*co*-4-methylstyrene) (BIMS).[1] For the samples where the benzylic bromide content was low (<0.75 mol %), a broad interface, approximately 350 Å thick, was observed. In all the samples studied previously, a persistent oscillation was observed in the NR data, which was interpreted as being due to a thin layer of PB. This layer was tenaciously attracted to the substrate even after being subjected to prolonged annealing at 150 °C. It is well established by now that the dynamical properties of polymers near attractive interfaces can differ from those of the bulk. Furthermore, the influence of the attractive surface has been observed by several authors to persist for distances far larger than the radius of gyration (R_g),[2−7] where the polymer chains involved have no direct contact with the attractive substrate. One of the earliest studies to show this effect was by Silberzan et al.,[2] where they studied liquid drops dewetting on a surface. They observed that the surface velocity of the droplets was at least an order of magnitude less than that of the bulk even though the height of the droplets was much greater than R_g. Close examination of the droplet morphology showed the existence of an adsorbed foot approximately one R_g thick. Their interpretation was to construct a two-fluid model where one fluid was pinned at the surface, confining the motion of the second fluid. Several authors have shown previously that the dynamics of polymers are reduced near an interacting interface. Frank, Zheng, and Lin[3−5] et al. all found that the polymer diffusion coefficient both in the surface plane[3] and perpendicular to the surface[4] was less than that in the bulk when the film thickness was less than approximately $10R_g$. A recent study on nanomechanical properties of unannealed poly(ethylene−propylene) films of varying thickness using scanning force microscopy also indicated that the effect of an attractive silicon surface extended out a distance of $7−10R_g$.[6] They postulated that even though the film was composed of a homogeneous polymer, rheologically the film responded as if it were composed of two fluids. One fluid had the normal viscosity expected at the measurement temperature, while the second layer was very viscous and resistant to flow. To interpret their results, the authors of both the rheological and tracer diffusion experiments postulated that the attractive interaction with the substrate permanently trapped a layer at the wall with $N^{1/2}$ contact points. These contacts formed an effective surface gel. This "gel" was able to trap other polymer chains within it that did not have direct contact with the wall, thus forming two fluids in one material. Even though this layer has been invoked in numerous theories for the past 10 years,[2−7] this is the first set of experiment designed to directly confirm its existence. More recently, long ranged interactions have also been reported in nanocomposite

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(1) Zhang, Y.; et al. Manuscript submitted to *Polymer*.
(2) Silberzan, P.; Leger, L. *Macromolecules* **1992**, *25*, 1267.
(3) Frank, B.; Gast, A. P.; Russell, T. P.; Brown, H. R.; Hawker, C. *Macromolecules* **1996**, *29*, 6531.
(4) Zheng, X.; Rafailovich, M. H.; Sokolov, J.; Strzhemechny, Y.; Schwarz, S. A.; Sauer B.; Rubinstein, M. *Phys. Rev. Lett.* **1997**, *79*, 241.
(5) Lin, E. K.; Kolb, R.; Satija, S. K.; Wu, W. L. *Macromolecules* **1999**, *32*, 3753.
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(7) Bruinsma, B. *Macromolecules* **1990**, *23*, 276.

systems.[8] In these systems, long-range interactions were used to explain the anomalous rheological characteristics in three dimensions when filler is present. A similar two-fluid mechanism for propagating the interactions has been proposed for these systems as well. Yet, even though this layer has long been postulated, it has never been directly observed.

Furthermore, there have been numerous reports in the literature of filler materials affecting the phase segregation of immiscible polymers.[9] Yet, there have not been any systematic studies on the effect of surface interactions on the miscibility, which can be determined from interfacial formation. Therefore, it is of interest to study the interfacial formation of immiscible polymer thin films as a function of the layer thickness, that is, the distance from the polymer/polymer interface to the substrate.
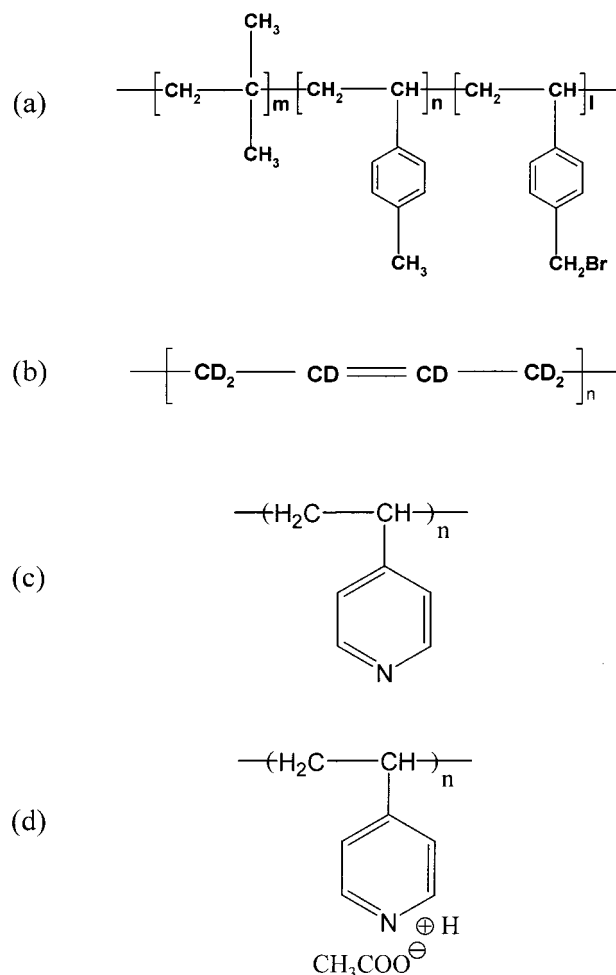
The technique we chose to use, neutron reflectometry (NR), uniquely probes the interfacial structure and dynamics of polymeric systems because of its excellent spatial resolution, high penetration depth, and nondestructive characteristics. In this work, we kept the chemical structure and the thickness of the second layer (BIMS) constant, varied the thickness of the substrate layer (dPB), and used NR to investigate the structure and kinetics of the interface formation between two elastomers, dPB and BIMS. We also controlled the effect of the silicon surface by introducing a noninteracting polymer layer, namely poly(4-vinylpyridine) acetate (P4VPAc), between the silicon surface and the dPB layer.

Experimental Section

Sample Preparation. BIMS is a synthetic random terpolymer of isobutylene (IB), *p*-methylstyrene (PMS), and *p*-bromomethylstyrene (BrPMS). The molecular structures of BIMS, dPB, P4VP, and P4VPAc polymers are shown in Figure 1. The characteristic data of three BIMS terpolymers and dPB, P4VP, and P4VPAc homopolymers are listed in Table 1. BIMS terpolymers were provided by ExxonMobil Chemical Corp., Baytown, TX. Up to 10 mol % PMS content, BIMS polymers are elastomeric in nature with low T_g ($-50\ °C$).[10] The polydispersity of these commercial BIMS polymers is in the range 2.5−2.8. P4VP and dPB homopolymers were purchased from Polymer Source Inc., Montreal, Canada. The double-layer samples for NR experiments were prepared by a procedure reported previously.[1] Here we only briefly describe this process. A 1 cm thick and 7.6 cm diameter silicon substrate was cleaned and etched by hydrofluoric acid to obtain a hydrophobic surface. A thin layer of dPB was spin coated at 2500 rpm from toluene solution onto the silicon substrate. The thickness of this layer, ranging from 230 to 730 Å, was controlled by varying the concentration of the solutions. The initial thickness was measured by ellipsometry. The second layer of BIMS, approximately 1 mm thick, was molded at 150 °C under a 3 metric ton load in a special mold for 1 h. The two layers were sandwiched just prior to the NR experiment.

For the triple layer sample, P4VP was first dissolved in acetic acid with a concentration of 2 mg/mL. This solution was then spin coated on a precleaned silicon substrate with a native oxide layer. The resultant poly(vinyl-4-pyridine) acetate (P4VPAc, Figure 1d) layer, approximately 89 Å thick, was annealed at 120 °C for 1 h in a vacuum oven to relax any strains and to remove the solvent introduced from the coating process. The second layer of dPB, approximately 200 Å thick, was spin coated on the first layer at 2500 rpm from a toluene solution. After being preannealed in a vacuum oven, the two layers were sandwiched with the BIMS layer for the NR experiment.

Neutron Reflectometry. To measure the interdiffusion between dPB and BIMS, the entire assembly in press was placed

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Figure 1. Molecular structures of (a) brominated poly(isobutylene-*co*-*p*-methylstyrene) terpolymer (BIMS), (b) deuterated polybutadiene (dPB), (c) poly(4-vinyl-pyridine), and (d) poly(4-vinyl-pyridine) acetate.

Table 1. Characteristics of Three Terpolymers (BIMS) and Three Homopolymers (dPB, P4VP, and P4VPAc) Used in This Study

| polymer	IB (mol %)	PMS (mol %)	BrPMS (mol %)	M_w (kg/mol)	M_w/M_n	SLD (10^{-6} Å^{-2})
BIMS-1	93	6.2	0.75	519	2.7	−0.2
BIMS-2	96	3.0	0.75	~450	~2.7	−0.2
BIMS-4	98	1.7	0.75	435	2.8	−0.2
dPB				223	1.03	6.0
P4VP				200	1.3	
P4VPAc				200	1.3	1.3

in an oven and annealed in a vacuum of 10^{-3} Torr at 150 °C for prescribed times. Since this temperature is well above T_g of both polymers, a PTFE (poly(tetrafluoroethylene)) ring attached to an adjustable clamp was used to maintain the shape of the samples and minimize the flow of the polymers during annealing. After being annealed for prescribed times, the samples were quickly quenched in air to room temperature. The PTFE ring and the clamp were subsequently removed before NR measurements.

The sandwiched wafers were then mounted on the horizontal sample stage at the NG-7 reflectometer at the Center for Neutron Research (NCNR), the National Institute of Standards and Technology (NIST). The press for annealing and the specular NR geometry are shown in Figure 2. The neutron beam enters through the 1 cm thick silicon wafer in the q_{in} direction and then is reflected from the BIMS/dPB interface and is subsequently detected in the q_{out} direction. In this study we examined eight double-layer samples. The compositions are tabulated in Table 2. We will hereafter mention these bilayers as samples A−H.
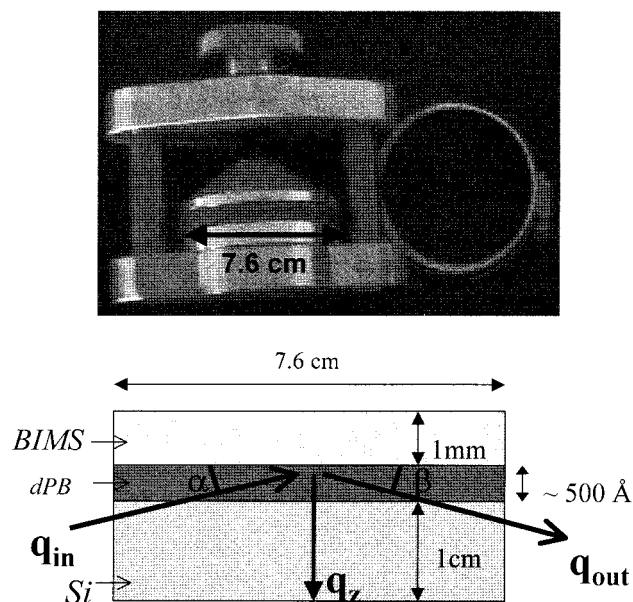
Figure 2. (a) Photograph of the entire sample chamber assembly used for annealing the sandwiched wafers. The PTFE ring is used to ensure that the heated polymer remains inside the compression zone of the mold. (b) Typical geometry of the specular neutron reflectivity setup. A thin dPB film is spun cast onto a thick silicon wafer. A thick disk of BIMS is placed on top of the silicon wafer. The neutron beam enters through the silicon wafer in the q_{in} direction. The beam is reflected from the dPB/BIMS interface and is detected in the q_{out} direction.

Table 2. Structure and Composition of Seven Bilayer Samples and One Trilayer Sample

| sample designation | lower layer(s) | | top layer |
	polymer	thickness (Å)	BIMS type
A	dPB	730	BIMS-1
B	dPB	500	BIMS-1
C	dPB	350	BIMS-1
D	dPB	230	BIMS-1
E	dPB	500	BIMS-2
F	dPB	350	BIMS-4
G	dPB	230	BIMS-2
H	P4VPAc/dPB	89/200	BIMS-1

The details of the NR technique and data analysis can be found in a review by Russell.[11] Here we only describe the experiments and data fitting results.

Small Angle Neuron Scattering (SANS). BIMS-1 (0.3 g) and dPB (0.7 g) were mixed in a toluene solution. After the solvent was evaporated, the remaining polymer mixture was placed in a sample holder. The final shape of the sample is circular with a thickness of 1 mm with the flat faces perpendicular to the neutron beam. This path length was chosen to ensure the best balance between the scattering intensity and attenuation. Otherwise, the samples are considered isotropic with no preferred orientation. The SANS experiment was performed at the Center for Neutron Research (NCNR), the National Institute of Standards and Technology (NIST), in Gaithersburg, MD. A neutron wavelength of 6 Å was used, with two collimation configurations. One has a sample−detector distance of 2.9 m, measuring a q range of 0.03−0.2 Å^{-1}, where q is the momentum transfer. The other has the sample−detector distance set at 15.2 m, measuring a q range from 0.003 to 0.04 Å^{-1}. Standard samples were used to calibrate the instrument, so all intensities measured were on the absolute scale of scattering cross section per unit volume (units of inverse centimeters).

Results and Discussion

Figure 3 shows the reflectivity, R, profiles obtained for bilayer sample A after annealing at 150 °C for different
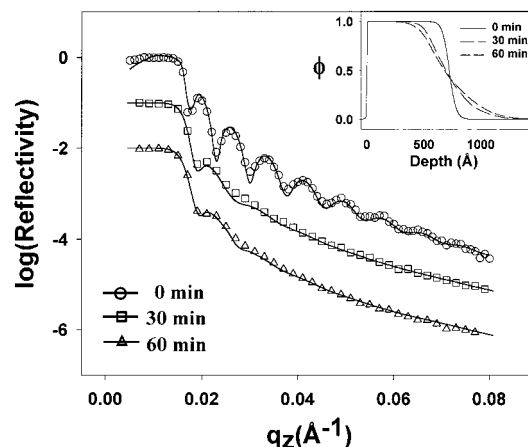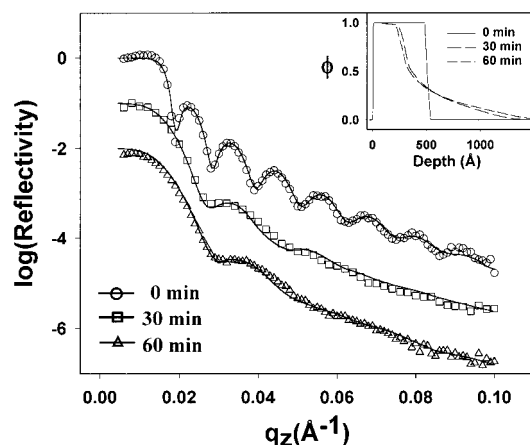

Figure 3. Neutron reflectivity data for different annealing times of the bilayer sample with a lower layer (dPB) 730 Å thick and an overlayer (BIMS-1) 1 mm thick. The solid lines represent the best fits to the experimental data. The inset shows best-fit profiles of dPB volume fraction as a function of distance from the silicon surface.

times, plotted as log R versus q_z, where $q_z = (4\pi/\lambda) \sin \theta$ and q_z, λ, and θ are the incident neutron wave vector, neutron wavelength, and incident angle, respectively. The initial thickness of the dPB layer is approximately 730 Å with a PB/BIMS interface, $w = 60$ Å. It should be noted that the curves for different annealing times in all the figures are vertically shifted for clarity. The high-frequency oscillations, which persist to approximately $q_z = 0.07$ Å^{-1}, indicate that, prior to annealing, the PB/BIMS interface is sharp. Annealing for 30 min causes most of the oscillation to disappear, indicating that the interface has broadened. Not much change in the profile results after further annealing for a total of 60 min, indicating that the profile has reached equilibrium. The model used to fit the data is shown in the inset to Figure 3. From the figure we see that prior to annealing the profile is fit by a single layer model of dPB with an error function interface with the BIMS, which is assumed to be an infinite medium. The parameters used in the fitting were described as follows: the thickness of the dPB layer (d_1), the PB/BIMS interfacial width (w), the thickness of the silicon oxide layer (d_2), the Si/SiO$_2$ roughness (σ_1), and the SiO$_2$/dPB roughness (σ_2). SLD values of the polymers are listed in Table 1. It should be noted that the reflectivity curve is determined primarily by d_1 and w in this system. Due to the HF treatment, the values of σ_1, σ_2, and d_2 are very small, that is, 6, 6, and 15 Å, respectively. After annealing, we observe that a low-frequency oscillation persists in the data. To fit this oscillation, it was necessary to add another dPB layer of thickness d_0 which was immobilized at the substrate. This layer formed a narrow interface with the mobile dPB layer. An asymmetric profile was found to produce a better fit to the reflectivity data at high q_z than a symmetric profile. This asymmetry is partially due to the adsorbed layer and to the fact that the BIMS has a relatively large polydispersity. At 30 min of annealing, the total BIMS/PB interface is approximately 300 Å. Due to the asymmetry of the diffused dPB volume fraction profile, we use the interquartile width, that is, the distance from the dPB volume fraction $\phi = 0.25$ to $\phi = 0.75$, as the total PB/BIMS interfacial width.[12] The thickness of the adsorbed layer d_0 is approximately 370 Å, or $3R_g$, where $R_g = 140$ Å is the radius of gyration for

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Figure 4. Neutron reflectivity data for different annealing times of the bilayer sample with a lower layer (dPB) 500 Å thick and an overlayer (BIMS-1) 1 mm thick. The solid lines represent the best fits to the experimental data. The inset shows best-fit profiles of dPB volume fraction as a function of distance from the silicon surface.
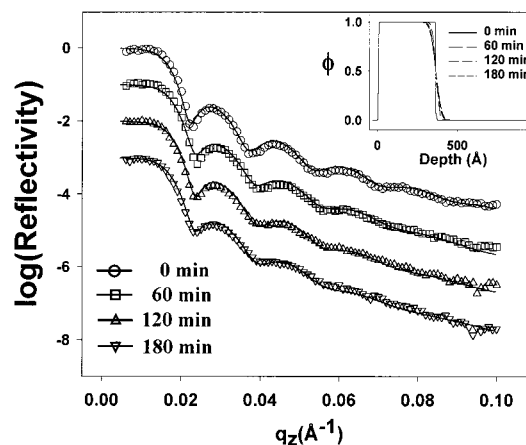
dPB of $M_w = 223\,000$. From previous contact angle data we established that the HF stripped silicon surface has a dispersive energy ($\gamma_{SiO} = 44$ dyn/cm) higher than that for dPB ($\gamma_{PB} = 24$ dyn/cm);[13] hence, dPB is adsorbed onto the silicon surface.

A similar result was observed for sample B, in which the original thickness of the dPB layer was reduced to approximately 500 Å. The reflectivity data shown in Figure 4 are qualitatively similar to the data shown in Figure 3 except that the amplitude of the remnant oscillation is higher. The initial interface between dPB and BIMS prior to annealing is sharp, with the best fit by one layer model yielding a value of 30 Å. The interface broadens significantly after annealing for 30 min with minimal further change after annealing for a total of 60 min. The same two-layer model is used to fit the diffused data. The interfacial width obtained, $w = 340$ Å, is comparable to the value observed in the previous sample (A). The thickness of the adsorbed layer, $d_0 = 240$ Å, and the interfacial width, $w = 340$ Å, did not change significantly with dPB layer thickness.

A large change in the spectrum is observed if we reduce the thickness of the dPB even further to 350 Å. The data are shown in Figure 5. From the figure we see that the Kiessig fringes are only slightly attenuated even after annealing for 180 min. These data can be fit by a simple error function profile with an interface of 20 Å for the unannealed sample, which broadened only to $w = 40$ Å after annealing for 180 min. If we decrease the thickness even further to 200 Å, we obtain similar profiles. The data are shown in Figure 6, and the dPB volume fraction profiles used to fit them are shown in the inset. In this case $w = 15$ and 25 Å, for the unannealed and annealed samples, respectively.

Similar results were obtained from bilayer samples of dPB and BIMS with the same bromide level but lower PMS content. The data from a bilayer sample with a 500 Å dPB layer are shown in Figure 7. From the figure we see that the interfacial width broadens to $w = 320$ Å within 120 min. When the dPB layer thickness is reduced to 350 or 220 Å (Figures 8 and 9), the interface remains narrow at approximately 30 Å.

The equilibrium interfacial width is plotted as a function of dPB thickness in Figure 10 for the different BIMS

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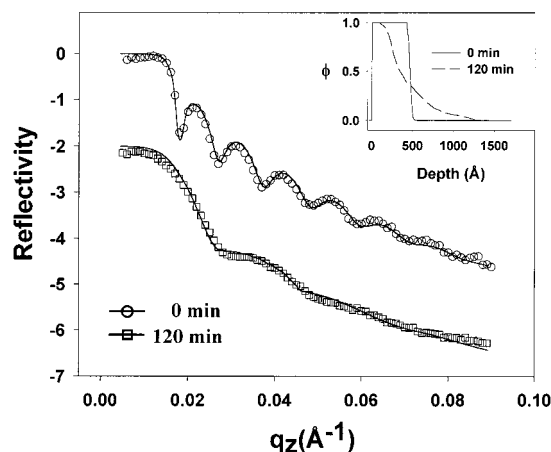

Figure 5. Neutron reflectivity data for different annealing times of the bilayer sample with a lower layer (dPB) 350 Å thick and an overlayer (BIMS-1) 1 mm thick. The solid lines represent the best fits to the experimental data. The inset shows best-fit profiles of dPB volume fraction as a function of distance from the silicon surface.
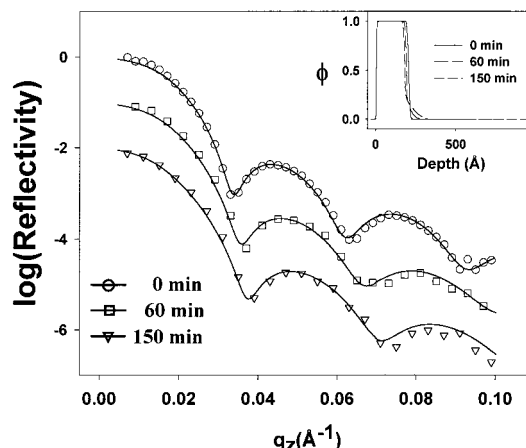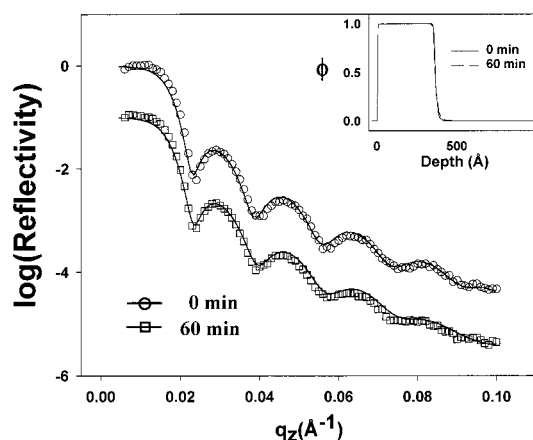

Figure 6. Neutron reflectivity data for different annealing times of the bilayer sample with a lower layer (dPB) 230 Å thick and an overlayer (BIMS-1) 1 mm thick. The solid lines represent the best fits to the experimental data. The inset shows best-fit profiles of dPB volume fraction as a function of distance from the silicon surface.

samples. From the figure we can see that in all cases when the dPB layer is less than 350 Å the interface between dPB and the BIMS matrix is very narrow. Since the interfacial interactions cannot change χ between the monomers, the narrowing must be a result of surface pinning. The radius of gyration for dPB of $M_w = 223$K is $R_g = 140$ Å. A layer of thickness $2R_g \sim 280$ Å therefore corresponds to a monolayer of dPB where each chain has on average $N^{1/2}$ monomers in contact with the silicon surface. Since no motion is observed, we can conclude that these contacts form strong bonds with the surface which prevent center of mass diffusion of the whole chain. The nature of the interaction between dPB monomers and SiH is not known, though it is clearly larger than the van der Waals interaction. This observation is consistent with previous measurements of Zhao *et al.*,[13] who showed that poly(ethylene−propylene) (PEP) will dewet a hydrophilic native oxide covered silicon substrate (dispersive $\gamma = 36.5$ dyn/cm) whereas the film will wet a hydrogen passivated hydrophobic silicon substrate where the dispersive energy has increased to $\gamma = 44$ dyn/cm. Decreasing the thickness further to 230 Å simply compresses the layer even closer to the interface and the interfacial width or the diffusion does not change. An abrupt change in the interfacial width

Figure 7. Neutron reflectivity data for different annealing times of the bilayer sample with a lower layer (dPB) 500 Å thick and an overlayer (BIMS-2) 1 mm thick. The solid lines represent the best fits to the experimental data. The inset shows best-fit profiles of dPB volume fraction as a function of distance from the silicon surface.
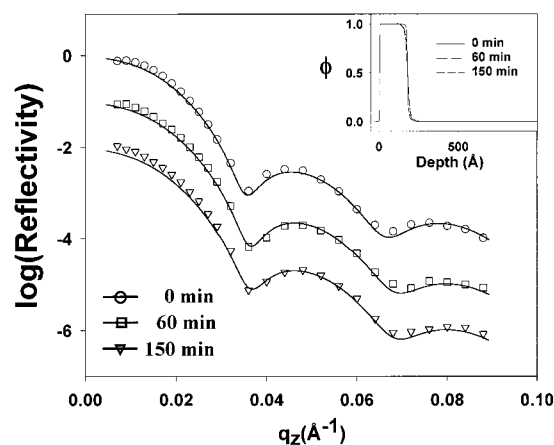

Figure 8. Neutron reflectivity data for different annealing times of the bilayer sample with a lower layer (dPB) 350 Å thick and an overlayer (BIMS-3) 1 mm thick. The solid lines represent the best fits to the experimental data. The inset shows best-fit profiles of dPB volume fraction as a function of distance from the silicon surface.

occurs when the dPB layer thickness is larger than $3R_g$ ~ 500 Å. Here we see from Figure 10 that the interfacial width increases by an order of magnitude to 350 Å. This value is unchanged when we increase the dPB thickness to 730 Å. To determine if this is the equilibrium value as determined by the Flory−Huggins interaction parameter for the system, or if the interfacial width still increases with distance from the silicon substrate, we use SANS to probe the intrinsic width in a bulk blend of BIMS-1/dPB after annealing the blend at 150 °C for 3 h. The data have a negative deviation from Porod law, indicating a diffuse interface. Using eq 18 in a reference by Koberstein et al,[14] we obtained the interface width $w = 350$ Å, which was plotted as a triangle in Figure 10:

$$I = (16\pi^4 K_p/q^4)(1 - w^2 q^2/12)$$

where I is the intensity, K_p is a q independent value, and q is the momentum transfer. This indicates that the equilibrium value is reached after sufficient annealing time (>120 min) once the dPB chains are no longer pinned

Figure 9. Neutron reflectivity data for different annealing times of the bilayer sample with a lower layer (dPB) 230 Å thick and an overlayer (BIMS-2) 1 mm thick. The solid lines represent the best fits to the experimental data. The inset shows best-fit profiles of dPB volume fraction as a function of distance from the silicon surface.
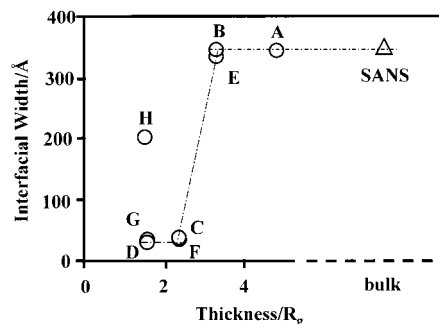

Figure 10. Equilibrium PB/BIMS interfacial thickness for samples A to H and the bulk SANS sample plotted as a function of dPB layer thickness normalized by R_g.

by the substrate. Since the intrinsic interfacial region is no larger than a dPB monolayer, we cannot probe longer-range effects in this system.

To confirm that the interfacial narrowing was only due to interactions with the substrate, we measured the interfacial width in a sample where the interactions were screened. Screening was accomplished by spin casting a thin (89 Å thick) monolayer of P4VP ($M_w = 200$ kg/mol, $R_g = 107$ Å) directly on the silicon surface from acetic acid. The layer was then annealed in order to ensure that all chains had some hydrogen bonds to the substrate.[15] P4VP is insoluble in toluene and highly immiscible with dPB. We therefore were able to spin cast and anneal a 200 Å thick layer of dPB directly on the P4VP surface. Figure 11 shows the NR data when the dPB layer was sandwiched with BIMS. From the figure we can see that the interface is no longer narrow even though the dPB layer is smaller than $2R_g$ (Figure 10). The initially sharp interface decays rapidly after 30 min of annealing in a manner similar to that for the thicker dPB layers. Even the remnant oscillation is seen to vanish after 150 min of annealing. The disappearance of this layer was not observed in any of the previous samples where the dPB was annealed in contact with the bare silicon surface. The inset shows the model used to obtain the best fit to the data. From the figure we can see that the volume fraction of dPB at the interface is no longer unity and the interfacial width has broadened to approximately 200 Å. Hence, the van der

(14) Koberstein, J. T.; Morra, B.; Stein, R. S. *J. Appl. Crystallogr.* **1980**, *13*, 34.

(15) The acetic acid molecules form complexes with P4VP and thus inhibit chemical reaction of the P4VP layer.
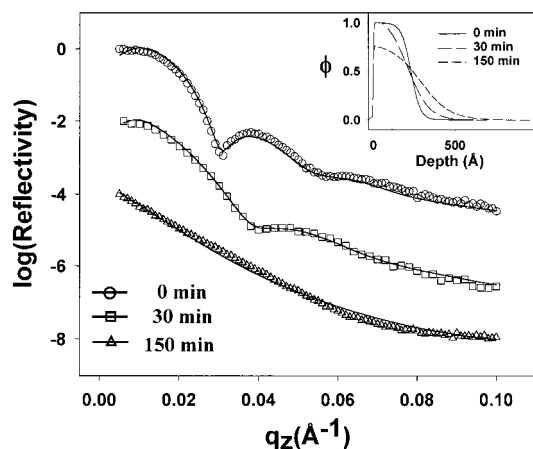
Figure 11. Neutron reflectivity data for different annealing times of the trilayer sample with a lower layer (P4VPAc) 89 Å thick, a middle layer (dPB) 200 Å thick, and an overlayer (BIMS) 1 mm thick. The solid lines represent the best fits to the experimental data. The inset shows best-fit profiles of dPB volume fraction as a function of distance from the silicon surface.

Waals forces which are the only interactions between PS and P4VP are insufficient to keep the polymer chains from diffusing into the BIMS matrix and establishing the equilibrium profile.

Since the T_g of dPB is well below room temperature (-20 °C), the strain induced from the spin casting process was relaxed after 1 h of preannealing. Consequently, the layer immediate to the silicon surface (trapped layer), about $1-3R_g$ thick, has at least one contact with the silicon surface. This adsorbed layer cannot be completely removed from the silicon surface even if the sample is annealed at 150 °C. Therefore, despite the difference in the diffusion rates, all reflectivity curves have remnant low-frequency oscillations even after prolonged annealing times. These remnant oscillations correspond to a thin layer of dPB chains that did not diffuse into the BIMS phase. This layer is found to be from 150 to 300 Å, or $1-2R_g$ thick.

Conclusions

In conclusion, we have found that an adsorbed polymer layer, approximately $2R_g$ thick, is always present at an attractive interface, in this case, a hydrophobic HF passivated silicon substrate. This observation confirms the existence of an immobile gel-like layer which was invoked by numerous authors[2−7] to explain the reduced dynamics and anomalous rheological properties of polymers at long distances from interactive substrates.

We have also shown the effect of an attractive substrate on the equilibrium interfacial width between immiscible polymers. In contrast to the reported hindrance of mobility which can extend for more than $10R_g$,[4] this effect is observed only for distances less than $3R_g$. Hence, unlike the rheological properties which are propagated by chains that are not in direct contact with the surface, the polymer/polymer interface is narrowed only when one of the layers is directly adjacent to the substrate.

The influence of the substrate was greatly reduced if the interactions were screened by coating the silicon substrate with an 89 Å thick P4VP layer.